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# Polyhedral Oligomeric Silsesquioxane (POSS) Styrene Macromers

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## ABSTRACT

Four polyhedral oligomeric silsesquioxane (POSS) macromers, $R_7Si_8O_{12}$Styrene (R = isobutyl, cyclopentyl, cyclohexyl or phenyl) containing a single polymerizable styrene unit were synthesized from the POSS-trisilanols $R_7Si_7O_9(OH)_3$ in high yield and purity. The base-assisted reaction to produce these macromers appears to be general for POSS-trisilanols of this type. However, in some cases it may be necessary to control the rate at which base is present during reaction to prevent unwanted side reactions that decompose the trisilanol. Cyclohexyl, cyclopentyl and isobutyl substituted POSS-stryenes (at 30 weight % loadings) undergo free radical bulk polymerizations with styrene to produce polymers with an enhanced modulus above the glass transition temperature. The phenylPOSS-derivative is too insoluble in styrene to undergo this polymerization. The effect on modulus is more pronounced for the copolymers containing 30 weight % cycloalkylPOSS than that seen with isobutylPOSS. The effect of the group at the POSS cage on bulk polymer properties has been noted before and is presumed to arise from differences in polymer microstructure.

# INTRODUCTION

The emerging field of nanocomposites is undergoing enormous growth as many new materials are being prepared to exploit this area of promising research.[1] One key appears to be controlling the length scales at which the composite is formed. A combination of disparate organic and inorganic materials at length scales that are approaching molecular dimensions would perhaps generate the greatest control of bulk properties. For example, a hybrid combination of organic polymers with inorganic fillers might generate materials that combine the processibility and flexibility of typical organic thermoplastics with the high use temperature, modulus and oxidation resistance of inorganic ceramics.[2]

Our approach is to tether well-defined polyhedral oligomeric silsesquioxane (POSS) inorganics to a variety of organic thermoplastics in an effort to generate such nanocomposites.[3] A typical POSS comonomer is about 1.5 nanometers in diameter and has a spherical inorganic $Si_8O_{12}$ core surrounded by eight organic groups. POSS is unique in that just one of these groups can be made reactive for polymerizations with organic monomers, while the other seven unreactive groups solubilize the inorganic core and allow for a degree of control over the interfacial interaction between the POSS and a polymer matrix.

Some work has already been published on solution polymerized POSS-styryl materials;[4] here we are detailing the synthetic procedures for making four different

POSS-styrene macromers. Each macromer has a single styrene unit for polymerizing and either cyclopentyl, cyclohexyl, isobutyl or phenyl groups attached to the inorgnic core. We also show preliminary data on bulk polymerizations in styrene monomer and the dynamic mechanical analysis of three different POSS-styrene materials.

## EXPERIMENTAL

### General Information

Solvents such as THF, ether and hexane were dried by passage through activated alumina columns.[5] Triethylamine was dried by refluxing over sodium metal and distilled prior to use. Bromostyrene was used as received and styrene was purified by passing through an inhibitor removal column, then vacuum transferred to a flask, freeze pump thawed three times and stored in a freezer under nitrogen. The POSS-trisilanols were either synthesized according to the literature methods[6] (**1b** and **1c**) or obtained from Hybrid Plastics Inc.[7] (**1a** and **1d**). All NMR spectra were collected on either a Bruker 300 or 400 MHz instrument and obtained from $CDCl_3$ solutions. $^1H$, $^{13}C$ and $^{29}Si$ NMR spectra (reported in ppm using the $\delta$ scale) were referenced to residual $CHCl_3$ at 7.26 ppm, to $CDCl_3$ at 77.0 ppm, and to external $SiMe_4$ at 0 ppm, respectively. HPLC were obtained on a HP 1090 Liquid Chromatograph by injecting 10 $\mu$L of a 5 ppt sample onto a polyvinylalcohol-silicagel column and eluting at 1 mL / minute using a 5 vol % THF /

95 vol % cyclohexane mobile phase and a Varex MKIII evaporative light scattering detector.

**Styryltrichlorosilane**

This synthesis is a modification to a literature method.[8] Under rigorous air and water-free conditions, a 250 mL pressure equalizing addition funnel containing a THF (200 mL) solution of bromostyrene (50.0 g, 0.273 mole) was attached to a 500 mL round-bottom flask containing magnesium turnings (7.97 g, 0.328 mole) and 40 mL of THF. A small crystal of iodine was added to activate the magnesium. After the yellow color dissipated, a slow drop-wise addition of the bromostyrene solution was continued for approximately two hours; the stirred solution became hot but did not reflux (Note that chlorostyrene may be substituted for bromostyrene, but it is necessary to reflux the solution to get a good conversion to the Grignard reagent). After the reaction mixture cooled to room temperature, stirring was stopped to allow a black precipitate to settle from the solution of styrylmagnesium bromide. The Grignard reagent was then added over a one hour period via a wide-bore cannula to a well-stirred THF (160 mL) solution of distilled $SiCl_4$ (51 g, 0.30 mol) in a 500 mL round-bottom flask. This mixture was stirred for 16 hours at which time a fair portion of the magnesium salts had precipitated. Gentle warming redissolved some of the salts and enabled continual stirring. Filtration is not recommended at this point because of the solubility of magnesium salts in THF. All

the THF solvent was then removed from the flask under dynamic vacuum; the flask was kept at room temperature to aid this process. The product was extracted with dry hexane (400 mL) and completely separated from the insoluble magnesium salts by filtration. Removal of the hexane under dynamic vacuum yielded about 50 mL of crude styryltrichlorosilane. Dynamic vacuum distillation (Bp. ~52 °C @ <1mm Hg) gave a 63 % yield (41.0 g, 0.173mol) of pure product. $^1$H NMR: 7.80 (d, $^3J_{H-H}$ = 8.2 Hz, aromatic C-H, 2H), 7.54 (d, $^3J_{H-H}$ = 8.2 Hz, aromatic C-H, 2H), 6.77 (dd, $^3J_{H-H}$ = 17.6, 10.9 Hz, vinyl C-H, 1H), 5.91 (d, $^3J_{H-H}$ = 17.6 Hz, $^2J_{H-H}$ = 0.6 Hz, vinyl C-H, 1H), 5.44 (d, $^3J_{H-H}$ = 10.9 Hz, $^2J_{H-H}$ = 0.6 Hz, vinyl C-H, 1H). $^{13}$C{$^1$H} NMR: 141.74, 133.44, 130.48, 126.22 (aromatic), 135.87, 116.90 (vinyl). $^{29}$Si{$^1$H} NMR: -1.2.

**Preparation of $R_7Si_8O_{12}$(Styryl): 2b R = c-$C_5H_9$, 2c R = c-$C_6H_{11}$, 2a R = i-$C_4H_9$**

The same procedure can be used for preparing cyclopentyl, cyclohexyl or isobutyl-substituted POSS-styrene; cyclopentyl substituted POSS-styrene, **2b**, is given as an example. Under a dry nitrogen atmosphere, a pressure equalizing addition funnel containing a THF (200 mL) solution of styryltrichlorosilane (27.18 g, 0.114 mole) was attached to a 1 liter round-bottom flask filled with a THF (500 mL) solution of (c-$C_5H_9$)$_7Si_7O_9$(OH)$_3$, **1b** (95.39 g, 0.109 mole) and NEt$_3$ (36.38 g, 0.360 mole). As the silane was slowly added over two hours to the vigorously stirred solution, copious amounts of NEt$_3$HCl precipitated from the solution. After stirring under nitrogen for 16

hours the remainder of the procedure was carried out in air. The suspension was filtered and the $NEt_3HCl$ precipitate was washed well with diethyl ether. The combined organic filtrate was washed with water (100 mL), 1 M HCl (100 mL), water (100 mL), brine (100 mL), dried over $MgSO_4$, filtered, and most of the organic solvent removed under vacuum. The resulting thick slurry was slowly poured into well-stirred methanol (400 mL) to fully precipitate the product, which was collected on a glass frit and air-dried to give a 90 % yield of product (98 g, 0.098 mol). $^1H$ NMR: 7.65 (d, $^3J_{H-H}$ = 8.0 Hz, aromatic C-H, 2H), 7.42 (d, $^3J_{H-H}$ = 8.0 Hz, aromatic C-H, 2H), 6.74 (dd, $^3J_{H-H}$ = 17.6 Hz, 10.9 Hz, vinyl C-H, 1H), 5.81 (dd, $^3J_{H-H}$ = 17.6 Hz, $^2J_{H-H}$ = 0.8 Hz, vinyl C-H, 1H), 5.30 (d, $^3J_{H-H}$ = 10.9 6 Hz, $^2J_{H-H}$ = 0.8 Hz, vinyl C-H, 1H), 1.76 (m, $Cp-CH_2$, 14H), 1.56 (m, $Cp-CH_2$, 42H), 1.02 (m, Cp-CH, 7H). $^{13}C$ NMR: 139.22, 134.32, 131.66, 125.42 (aromatic), 136.90, 114.56 (vinyl), 27.36, 27.04, 26.98 ($Cp-CH_2$), 23.31 (Cp-CH). $^{29}Si$ NMR: -66.0 (3 Si-Cp), -66.4 (4 Si-Cp), -79.7 (1 Si-Styryl). Elemental analysis (calculated.): % C, 51.03 (51.46); % H, 7.22 (7.03). HPLC shows the compound to be >98 % pure.

**Data for $(c-C_6H_{11})_7Si_8O_{12}$(Styryl), 2c**

$^1H$ NMR: 7.65 (d, $^3J_{H-H}$ = 8.0 Hz, aromatic C-H, 2H), 7.44 (d, $^3J_{H-H}$ = 8.0 Hz, aromatic C-H, 2H), 6.75 (dd, $^3J_{H-H}$ = 17.6 Hz, 10.9 Hz, vinyl C-H, 1H), 5.82 (d, $^3J_{H-H}$ = 17.6 Hz, $^2J_{H-H}$ = 0.8 Hz, vinyl C-H, 1H), 5.30 (d, $^3J_{H-H}$ = 10.9 Hz, $^2J_{H-H}$ = 0.8 Hz, vinyl C-

H, 1H), 1.76 (m, Cy-CH$_2$, 35H), 1.25 (m, Cy-CH$_2$, 35H), 0.80 (m, Cy-CH, 7H). $^{13}$C

NMR: 139.23, 134.34, 131.54, 125.48 (aromatic), 136.88, 114.63 (vinyl), 27.52, 27.47,

26.93, 26.86, 26.69, 26.62 (Cy-CH$_2$), 23.22, 23.13 (Cy-CH). $^{29}$Si NMR: -68.2 (3 Si-

Cy), -68.5 (4 Si-Cy), -79.6 (1 Si-Styryl). Elemental analysis (calculated.): % C, 54.13

(54.50); % H, 7.92 (7.68). HPLC shows the compound to be >98 % pure.


**Data for (c-C$_4$H$_9$)$_7$Si$_8$O$_{12}$(Styryl), 2a**

$^1$H NMR: 7.63 (d, $^3J_{\text{H-H}}$ = 8.0 Hz, aromatic C-H, 2H), 7.42 (d, $^3J_{\text{H-H}}$ = 8.0 Hz,

aromatic C-H, 2H), 6.73 (dd, $^3J_{\text{H-H}}$ = 17.6 Hz, 10.9 Hz, vinyl C-H, 1H), 5.82 (d, $^3J_{\text{H-H}}$ =

17.6 Hz, vinyl C-H, 1H), 5.30 (d, $^3J_{\text{H-H}}$ = 10.9 Hz, vinyl C-H, 1H), 1.89 (m, Bu-CH, 7H),

0.97 (t, J = 6.8 Hz, Bu-CH$_3$, 42H), 0.64 (m, Bu-CH$_2$, 14H). $^{13}$C NMR: 139.24, 134.30,

131.27, 125.42 (aromatic), 136.84, 114.67 (vinyl), 25.72 (Bu-CH$_3$), 23.89 (Bu-CH),

22.53, 22.44 (Bu-CH$_2$). $^{29}$Si NMR: -67.16 (3 Si-Bu), -67.78 (3 Si-Bu), -67.86 (1 Si-Bu),

-80.44 (1 Si-Sty). Elemental analysis (calculated.): % C, 46.08 (47.02); % H, 7.76 (7.67).

HPLC shows the compound to be >98 % pure.


**Preparation of (C$_6$H$_5$)$_7$Si$_8$O$_{12}$(Styryl), 2d**

This inverse addition procedure was also successful for making the isobutyl-

substituted POSS-styrene. Under a dry nitrogen atmosphere, a THF (50 mL) solution of

NEt$_3$ (7.171 g, 70.87 mmol) was added over a 15 minute period to a THF (150 mL) solution of (C$_6$H$_5$)$_7$Si$_7$O$_9$(OH)$_3$, **1d**, (20.00 g, 21.47 mmol) and styryltrichlorosilane (5.357 g, 22.55 mmol). The solution was stirred overnight for 16 hours, then filtered (in air) to remove most of the NEt$_3$HCl. After washing the NEt$_3$HCl with diethyl ether, the filtrate was washed with water (20 mL), 1 M HCl (20 mL), water (20 mL), brine (20 mL), dried over MgSO$_4$, filtered, and most of the organic solvent removed under vacuum. The resulting thick slurry was slowly poured onto well-stirred methanol (100 mL) to fully precipitate the product, which was collected on a glass frit and air-dried to give a 97 % yield of product (22.08 g, 20.84 mmol). $^1$H NMR: 7.83 (m, *o*-phenyl C-H, 14H), 7.79 (d, $^3J_{H-H}$ = 8.0 Hz, styryl C-H, 2H), 7.48 (m, *p*-phenyl C-H, 7H), 7.42 (m, *m*-phenyl and styryl C-H, 16H), 6.76 (dd, $^3J_{H-H}$ = 17.6 Hz, 10.8 Hz, vinyl C-H, 1H), 5.85 (dd, $^3J_{H-H}$ = 17.6 Hz, $^2J_{H-H}$ = 0.8 Hz, vinyl C-H, 1H), 5.34 (dd, $^3J_{H-H}$ = 10.8 Hz, $^2J_{H-H}$ = 0.8 Hz, vinyl C-H, 1H). $^{13}$C NMR: 139.74, 134.49, 129.51, 125.67 (styryl), 136.64, 115.07 (vinyl), 134.20, 130.80, 130.14, 127.88 (phenyl). $^{29}$Si NMR: -77.92 (1 Si-Styryl), -77.98 (7 Si-Ph). HPLC shows the compound to be >98 % pure.


**Bulk Polymerizations**

The bulk polymerization of POSS-styrene monomers was carried out by dissolving 30 weight % of a POSS-styrene macromer, **2a-c**, (300 mg, 0.3 mmol) in

styrene (700 mg, 6.7 mmol), adding 0.25 mol % AIBN radical initiator (2.9 mg, 0.18 mmol) and heating the solution under nitrogen for 72 hours at 60 °C. This method was successful for isobutyl, cyclopentyl and cyclohexylPOSS only; the phenylPOSS derivative, **2d**, was too insoluble in styrene to undergo a bulk copolymerization. No attempt was made to purify these copolymers.

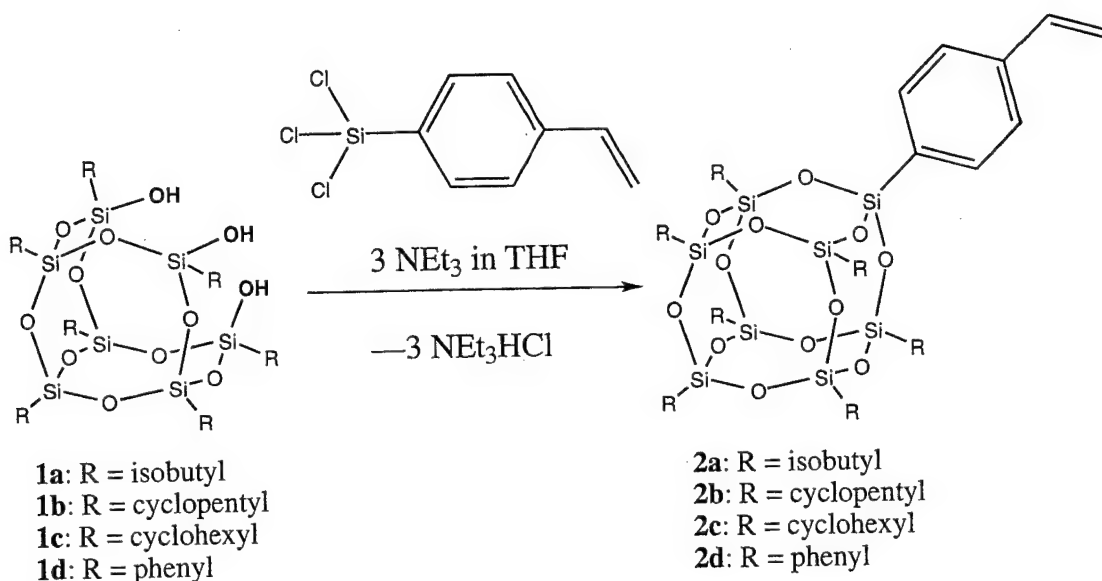## Dynamic Mechanical Analysis

Samples of the POSS-polystyrenes were melt pressed between aluminum sheets for 1 min at 150 °C and 10000 psi. After slow cooling, strips of nominal dimensions 8 mm length x 6.4 mm width x (0.2-0.4) mm thickness were cut. Dynamic mechanical temperature scans in dynamic tension were conducted on the strips in a Rheometrics Dynamic Mechanical Thermal Analyzer (DMTA). The samples were prestrained to 2 N (static force exceeding dynamic force by 50%) and heated at 2.5 °C/minute until 200 °C. The samples were noted to neck and draw at elevated temperatures.

## RESULTS AND DISCUSSION

### Synthesis

The synthesis of four monostyryl substituted POSS-macromers was achieved as shown in Figure 1. This type of corner capping reaction is virtually quantitative for a variety of monosubstituted trichlorosilanes, and is most often carried out in THF solution using a soft base such as triethylamine to both catalyze the reaction and to drive the

reaction forward by the production of an HCl salt.[6b,9] Several transformations of cyclopentyl and cyclohexyl POSS-trislanols (**1b,c**) have been previously reported;[10] this is the first report using isobutyl or phenylPOSS-trisilanol (**1a,d**).



**1a**: R = isobutyl
**1b**: R = cyclopentyl
**1c**: R = cyclohexyl
**1d**: R = phenyl

**2a**: R = isobutyl
**2b**: R = cyclopentyl
**2c**: R = cyclohexyl
**2d**: R = phenyl

**Figure 1.** The transformation of four POSS-trisilanols into POSS-styrene macromers.

In a typical corner capping reaction, the trisilanol and base are placed in a THF solution and a slow addition of a trichlorosilane gives an excellent yield of product. This was found to be true for isobutylPOSS-trisilanol **1a**, but was not the case for phenylPOSS-trisilanol **1d**. Instead of a single product, a myriad of compounds were formed as shown by HPLC and NMR spectroscopy. The problem was discovered to be caused by the NEt$_3$ catalyzing self-condensation of the phenylPOSS-trisilanol. In fact, while trisilanols **1a-c** are stable at room temperature in THF and NEt$_3$, trisilanol **1d** forms an ill-defined polymeric material.

This problem was solved by combining the phenylPOSS-trisilanol with the styryltrichlorosilane in THF solution, and then slowly adding in NEt$_3$ such that it is
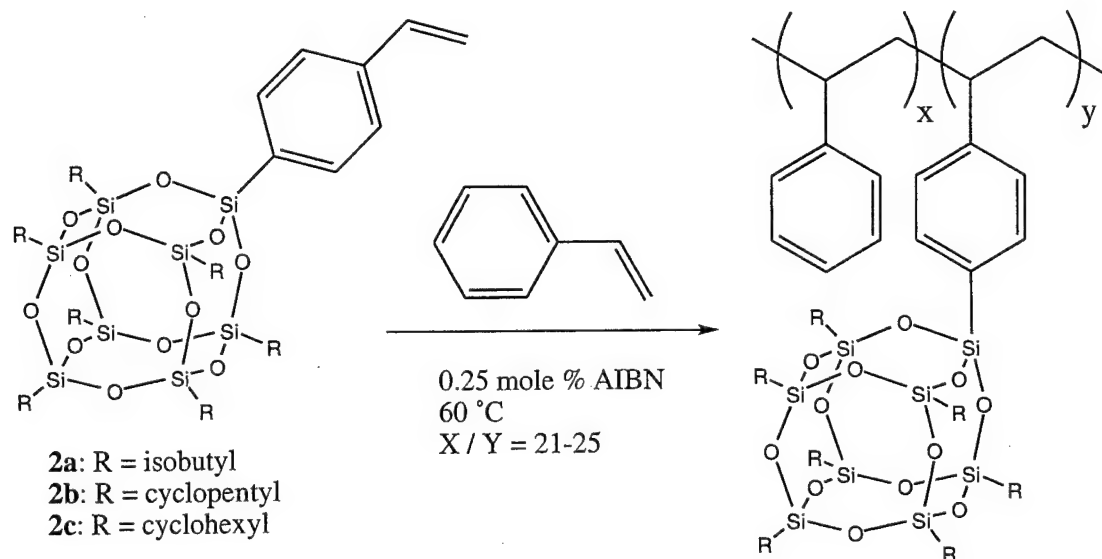
consumed by the formation of insoluble $NEt_3HCl$ as the reaction proceeds. Other chlorosilanes will also effeciently cornercap trisilanol **1d** using this inverse addition procedure.[11] A possible explanation for the reactivity of **1d** with $NEt_3$, is that the phenylPOSS-trisilanol is more acidic than its aliphatic analogs.[12] A higher acidity could yield an appreciable concentration of deprotonated trisilanol (in the presence of $NEt_3$) that could self condense if there is not enough chlorosilane present to react with. In support of this argument, the cyclic all-cis $(phenyl)_4Si_4O_4(OH)_4$ is reported[13] to decompose in the presence of triethylamine, while the cyclopentyl analog $(c\text{-}C_5H_9)_4Si_4O_4(OH)_4$ is stable under the same conditions.[14]

Evidence for **1d** having a higher acidty is obtained from $^1H$ NMR spectroscopy. The chemical shift of the trisilanols (in $CDCl_3$ and at the same concentration) comes at 7.8 ppm for **1d**, while the same broad OH peak is at 6.1 for **1a**, 5.0 for **1b**, and 6.0 for **1c**. All other factors being equal, a more acidic OH group would be expected to resonate in a more deshielded environment; of course there may also be a deshielding effect from the close proximity of neighboring phenyl groups which is not accounted for.

**Polymerization**

The bulk polymerization of styrene with 30 weight % of the various POSS-styrene macromers was carried out using AIBN as a radical initiator (Figure 2). Unlike the alkylPOSS-styrenes **2a-c**, the phenylPOSS-derivative **2d** was so insoluble in styrene that the resulting polymer was an opaque material embedded with unreacted POSS. Even at a low 10 weight % loading, this POSS macromer is too insoluble in styrene to effect

copolymerization. Studies are now underway to make copolymers using solution polymerization techniques. However, copolymers made with macromers **2a-c** were all translucent high molecular weight glassy materials. A 30 weight % loading of a POSS-styrene in styrene is approximately equivalent to 1 POSS moiety for every 22-26 monomers in the copolymer or approximately 4 mole % POSS (4.6% for **2a**, 4.3 % for **2b** and 3.9 % for **2c**).



2a: R = isobutyl
2b: R = cyclopentyl
2c: R = cyclohexyl

0.25 mole % AIBN
60 °C
X / Y = 21-25

**Figure 2.** The free radical copolymerization of three POSS-styrenes in styrene monomer.

This 4 mole % POSS loading in the copolymer results in dramatic changes to the glassy styrene matrix and is illustrated by dynamic mechanical analysis. After pressing the copolymers into thin sheets, strips were cut and subjected to DMTA under tension from room temperature up to 200 °C (Figure 3). It has been noted before that some solution polymerized POSS copolymers show increases to glass transition and, more

importantly, to use temperature.[15]  That is, POSS incorporation will sometimes lead to

formation of a rubbery plateau such that the polymer will have a significant modulus

even at temperatures above the glass transition.  In addition, the type of group on the

POSS cage (cylcopentyl or cyclohexyl) will dictate the size of this effect on the bulk

properties of the material.  Figure 3 illustrates clearly this POSS-group dependence.
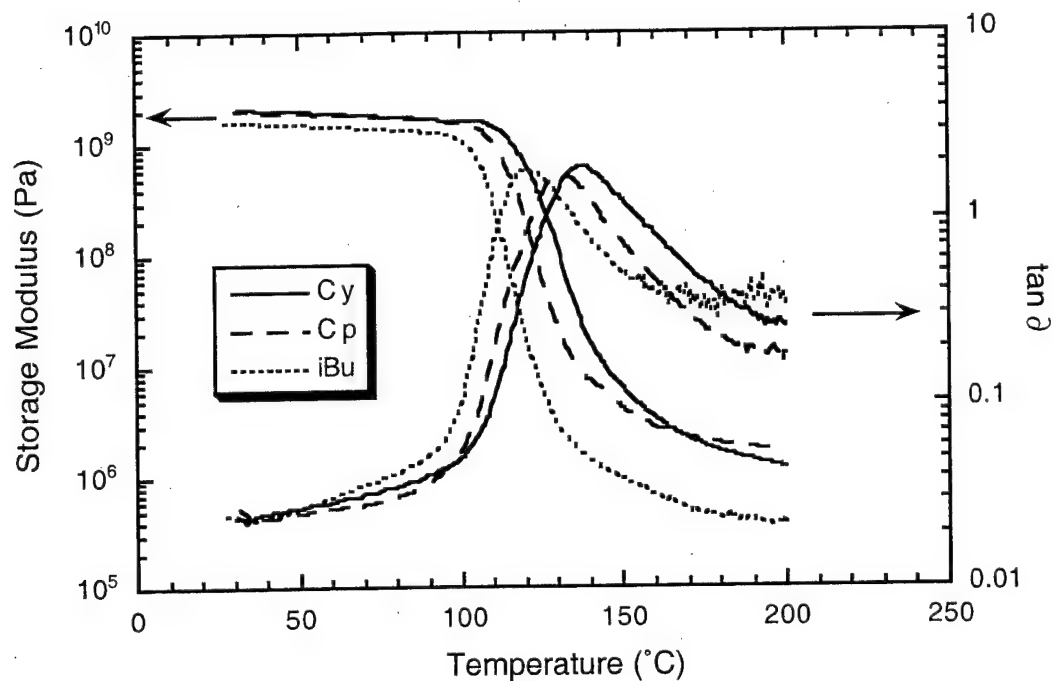


**Figure 3.** The dynamic mechanical spectra for three 30 weight % POSS-styrene

copolymers. Cy, Cp and iBu refer to the three types of copolymers containing cyclohexyl,

cyclopentyl or isobutylPOSS, respectively.

The modulus of these three polymers at room temperature are all very similar and

typical for glassy polymers.  However, 30 °C above the glass transition temperature the

modulus of the cyclopentyl and cyclohexylPOSS copolymers is still over $10^6$ Pa and significantly higher than that of the isobutylPOSS copolymer. The glass transition of each copolymer (obtained from the peak in tan $\partial$) is 120 °C for the isobutyl derivative, 131 °C for cyclopentyl derivative, and 138 °C for the cyclohexyl containing copolymer. Clearly, the alkyl group has a strong effect on the bulk properties of the copolymer. Property differences arising from a variation in these POSS-groups is a recurring theme for POSS copolymers and further study of this system is warranted. In particular, TEM images coupled with detailed DMA data over a range of % POSS incorporations may shed light on how the POSS groups affect polymer microstructure and bulk properties.

## CONCLUSIONS

A wide variety of substituted POSS-styrenes were synthesized in high yield and purity. The base-assisted reaction to produce these macromers appears to be general for any POSS-trisilanols. However, in some cases it may be necessary to control the rate at which base is present during reaction to prevent unwanted side reactions that decompose the trisilanol. Cyclohexyl, cyclopentyl and isobutyl substituted POSS-stryenes undergo free radical bulk polymerizations with styrene to produce polymers with an enhanced modulus above the glass transition temperature. This effect is much more prominent for the copolymers containing 30 weight % cycloalkylPOSS than that seen with isobutylPOSS. The effect of the group at the POSS cage on bulk polymer properties has

been noted before and is presumed to arise from differences in polymer microstructure. The packing of the POSS cages in the glassy matrix is strongly affected by the type of group on the POSS moiety. Further work on this aspect of POSS-polystyrenes is underway.

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